

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of Titanium

10 We, KAISER ALUMINIUM & CHEMICAL CORPORATION, a Corporation organized under the laws of the State of Delaware, United States of America, and having its office at 1924, Broadway, Oakland, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

15 This invention relates to a process for producing ductile titanium metal; and, more particularly, to such process wherein titanium chlorides are reacted to form titanium metal.

20 Titanium is known to be a metal of great strength and light weight and is rapidly coming to be recognized as very desirable in construction where these qualities are of particular importance, for instance, in aircraft manufacture. Various methods have been proposed for preparing the pure metal inasmuch as it occurs principally as the oxide, in rocks and ores, those methods including reduction of the oxide with aluminium, electrolysis of the oxide dissolved in fused calcium chloride, and conversion of the Ti values to tetrachloride, followed by direct reduction of titanium chlorides to the metal by reaction with hydrogen or with alkali or alkaline earth metals. The reduction of titanium tetrachloride to titanium by reaction with a metal such as magnesium, sodium, potassium or calcium has been so successful commercially as to clearly demonstrate the above advantageous uses for titanium metal.

35 However, it is a particular problem in this art to make ductile metal of high purity. Some of the known processes yield titanium which contains impurities that render the metal brittle and unworkable; whereas, in other processes, the principal disadvantage is that the impurities, though not so harmful with regard to ductility, are present in substantial and objectionable amounts and are extremely difficult to remove, requiring, for example, comminution of a mass of titanium product, followed by leaching and/or treatment at higher tempera-

[Price 3s. 6d.]

tures to volatilize off the undesired contaminants, such as the halides of the reducing metal. These treatment steps are expensive and time-consuming, resulting in increased costs of production and a high-priced metal. For instance, the grinding step alone is expensive and difficult because titanium is extremely tough, requiring special grinding devices.

55 It is an object of the present invention to provide a method for producing high purity, ductile titanium. It is a further object to provide a method for producing such titanium which is much less costly or expensive than hitherto known methods. It is a specific object 60 of this invention to provide a method for producing high purity, ductile titanium in compact form, especially suitable for further melting operations.

65 According to the present invention, ductile titanium is prepared by heating titanium trichloride in the presence of a stream of inert gas, at a temperature of from 550° C. to 650° C., to form titanium dichloride and titanium tetrachloride, and separately recovering 70 the titanium dichloride, while the titanium tetrachloride is removed as a vapour entrained in the stream of inert gas. The titanium dichloride which is recovered is then heated to a temperature of from 700° C. 75 to 1100° C. in the presence of a stream of inert gas to form titanium metal and titanium tetrachloride, and the titanium metal is separately recovered while the titanium tetrachloride is removed as a vapour by the stream of inert gas 80 The metal so recovered is in a particulate form especially suitable for melting and further operations, and is free of contaminants which if present would cause brittleness and non-workability. The metal obtained can be melted to 85 yield ductile, workable titanium.

The titanium trichloride can be prepared in any desired manner. A preferred method is reduction of titanium tetrachloride by reaction thereof in a reducing zone with titanium or 90 another metal which reacts with $TiCl_4$ to form $TiCl_3$ and a chloride of the reducing metal

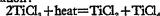
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which is volatile at the temperature of the reduction reaction, and which has a condensation point lower than that of the titanium trichloride produced. An excess of $TiCl_3$ is employed and the reduction zone is maintained at a temperature at which the $TiCl_3$ is carried off as a vapour by the stream of excess $TiCl_4$, i.e. at which the $TiCl_3$ has an appreciable vapor pressure. The $TiCl_3$ is condensed and separately recovered from the vapor stream after it leaves the reduction zone. The temperature of the reduction zone is advantageously at least $750^\circ C$. and is preferably from $750^\circ C$. to $950^\circ C$. In the reduction operation, the reducing metal is titanium a metal of which the chloride has a boiling point or condensation point lower than that of $TiCl_3$, as stated, and is preferably aluminium, zinc or titanium. Aluminium is especially suitable. Scrap titanium or titanium alloys or nonductile titanium can be re-worked in this manner. The reduction step described is particularly advantageous because the $TiCl_3$ and the chloride of reducing metal are volatile and are removed from the reducing zone, thereby producing $TiCl$ freed of the nonvolatile impurities in the starting materials. Likewise, the $TiCl_3$ is condensed from the issuing vapor stream and is thereby separated from the chloride of the reducing metal. The chloride of the reducing metal is preferably removed, as by condensation and separation, from the $TiCl_3$ which can then be recycled to the process. The reduction step may result in titanium trichloride which contains some titanium dichloride, but this is not objectionable. If, where zinc is the reducing metal employed, some zinc chloride condenses with the $TiCl_3$, it can be removed therefrom in any desired manner either before or after the first disproportionation step. The vapor stream after leaving the reduction zone is cooled to condense $TiCl_3$ therefrom, for example, to a temperature of from $450^\circ C$. to $600^\circ C$. The $TiCl_3$ may deposit as rather fine crystals when the issuing vapors are cooled, and it is advantageous to dilute the hot vapour with 5 to 10 volumes of an inert gas, such as argon, per volume of vapor, and then to cool to deposit larger crystals of $TiCl_3$. The inert gas should be preheated in order to maintain the temperature of the gaseous admixture above that at which $TiCl_3$ condenses.

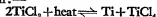
The trichloride or mixture of di- and trichlorides is introduced into a heating zone and is there heated at from $550^\circ C$. to $650^\circ C$. in the presence of a stream of an inert gas, for instance, a noble gas, such as argon. The inert gas contains vaporous or gaseous titanium tetrachloride, provided the partial pressure of $TiCl_4$ is less than the equilibrium partial pressure of this material for the disproportionation reaction at the temperatures employed. The trichloride can be heated in powder form, as obtained by the reduction process, for example,

but it can be formed into agglomerates prior to this heating step for convenience of handling. These agglomerates can be prepared, for example, by pelleting or briquetting. In this heating step, the crystal size of the product obtained is favorably influenced, i.e. the crystals are larger, when the disproportionation is carried out slowly, for instance, when the temperature is maintained at about $600^\circ C$., preferably from $575^\circ C$. to $625^\circ C$. The reaction is belived to proceed according to the following equation:—



The titanium tetrachloride has a substantial equilibrium partial pressure at the temperature of the reaction and passes out of the reaction zone with the stream of inert gas. It has also been found that some of the $TiCl$ tends to vaporize off under the reaction conditions and it is again deposited when the effluent vapors are cooled to its condensation or solidification temperature, at which time the deposit is recycled to the reaction zone. The effluent vapors issuing from this first heating or disproportionation zone (after removal of deposited $TiCl_3$, if any) are conducted to a condensation or cooling zone where they are cooled to a temperature at which $TiCl_3$ condenses. The condensed $TiCl_3$ is then separately recovered and is sent to storage or, preferably, reduced to $TiCl_2$ in any desired manner and is then reintroduced into the reaction system to be disproportionated.

The titanium dichloride produced by the first heating step is maintained under a stream of inert gas and is subjected to a second heating or disproportionation step wherein it is heated to disproportionate at from $700^\circ C$. to $1100^\circ C$., with formation of titanium metal and titanium tetrachloride. It is believed that this reaction proceeds according to the following equation:—



The titanium dichloride can be heated in powder form as obtained from the first disproportionation reaction and ductile titanium is thereby obtained. It is preferred, however, to form agglomerates of the $TiCl_2$ by pelleting or briquetting, preferably under pressure, because when the agglomerated material is disproportionated the final pellet or briquette of metal is quite dense and is in excellent condition for melting and handling operations. The optimum temperature in the second heating step is from $1000^\circ C$. to $1100^\circ C$. for the most rapid and complete reaction. It is preferred to introduce into this zone a stream of inert gas, e.g. argon, which contains not over 2 mm., or, for optimum operation, not over 1 mm., partial pressure of $TiCl_4$. It will be understood that higher concentrations of $TiCl_4$ can be present but in such instances the highest efficiency of the process is not attained.

In this second disproportionation step, the $TiCl_4$ which is formed enters the vapor phase

and is withdrawn with the argon or other inert gas. The titanium metal is solid at the temperature of the reaction and remains as a residue. In practice, it is observed that some $TiCl_3$ also enters the vapor phase. This substance may form by reaction between the dichloride and some of the tetrachloride which is formed, or by reaction between the titanium and some of the tetrachloride. Whatever its source, it deposits from the effluent gases as they are cooled, and is preferably recycled to the system.

It is advantageous to increase the temperature in the second heating zone to from 1000° C. to 1100° C., or to carry out the reaction at this range, in order to ensure complete reaction and to drive off all titanium chlorides from the metal residue.

The titanium obtained by the process of the present invention is characterized by freedom from the impurities oxygen and nitrogen, which would impart brittleness, and by its workability. The metal is in either powdered form or in the form of agglomerates of selected sizes, which latter is a very advantageous feature of this invention because the metal can be easily handled and subjected to the usual melting and alloying operations. Grinding of an extremely hard massive Ti sponge is avoided. It is especially advantageous to briquette or agglomerate the $TiCl_3$, which may also contain a minor amount of finely divided Ti metal, under pressure prior to disproportionation thereof because compact metal in agglomerates of desired sizes is thereby obtained.

The inert gas employed is substantially free of impurities causing brittleness in the metal product, especially nitrogen and oxygen. The inert gas can be, for example, a noble gas such as helium, argon, neon. Argon, for example, which contains not over about 0.05% impurities is now available commercially and after gettering is useful in this invention. Mixtures of inert gases can be employed. The inert gas is employed as a sweep gas and in sufficient amount to maintain the partial pressure of volatilized $TiCl_4$ at less than the equilibrium partial pressure at the temperature of the reaction zone, and the partial pressure of any $TiCl_3$ present in the entering gas should be substantially below such equilibrium partial pressure. The inert gas is recycled for maximum efficiency, but $TiCl_3$ must be largely removed therefrom prior to reintroduction of the gas into the disproportionation zones. The gas stream issuing from the first disproportionation zone comprises the inert gas, e.g. argon, and vaporized $TiCl_4$ which is produced in the reaction. This gas mixture is cooled, preferably to room temperature, to condense the $TiCl_4$ and the liquid $TiCl_4$ is withdrawn and can be recycled to a reduction zone as desired, while the inert gas, containing not more than the equilibrium partial pressure and preferably not

over 10 mm. partial pressure of $TiCl_3$, is returned to the disproportionation zone. Alternatively, the $TiCl_3$ can be removed by compression of the gas mixture, followed by release of pressure, if desired. The gaseous 70 mixture comprising inert gas and titanium tetrachloride, which issues from the second disproportionation zone, is treated to remove $TiCl_3$, e.g. is cooled to condense $TiCl_3$, e.g. preferably to a temperature of about -15° C. 75 and the content of $TiCl_3$ in the gas is preferably reduced in any desired manner to not over 2 mm., or, as optimum, not over 1 mm., partial pressure, to enable faster reaction and to avoid or minimize back reaction, i.e. to enable 80 more complete removal of chlorides. The inert gas so purified is then introduced again into the second disproportionation zone. A portion of this purified gas can also be fed to the first disproportionation zone, if desired. Make-up 85 inert gas can be added from time to time, as necessary, to either or both heating stages to supplement for losses normally occurring in such recirculations. It is also, advantageous to treat the withdrawn inert gas, from which 90 $TiCl_4$ has been largely removed, with a "getter", for example, titanium, to remove any contaminants such as oxygen or nitrogen which it may have taken up during operation. Scrap titanium or titanium alloy can be used for this 95 purpose.

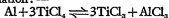
It is a particular advantage of the process of the present invention that the inert gas employed prevents the contamination of the product due to reaction of the active titanium chlorides with oxygen or moisture, or to the occlusion of other reactive gases. It is also an advantage that the presence of the inert gas enables the disproportionation reaction to proceed at normal pressures, which is desirable 105 not only from the standpoint of equipment design but also from that of operating techniques. It is a further advantage that the inert gas can be purified in the course of operations in a rapid and fairly inexpensive manner, with respect to $TiCl_4$ vapor, by cooling, by passing through a water-cooled condenser or, where cooling to -15° C. is desired, by refrigeration according to known procedures; and, as oxygen or nitrogen may be picked up from impurities present in the starting material, by passing the gas over a "getter" which, as stated above, can advantageously be titanium metal preferably of large surface, i.e. sponge or finely divided. 120

The following examples will demonstrate more clearly the mode of operation of this invention.

EXAMPLE I.

Titanium trichloride is prepared by reacting liquid aluminum at 850° C. with excess $TiCl_4$ vapor, at atmospheric pressure, to form a vaporous mixture comprised principally of titanium trichloride, aluminum chloride and $TiCl_4$. A minor amount of $TiCl_3$ is also usu- 130

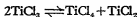
ally present. The reaction goes rapidly and is carried out by flowing the $TiCl_4$ over the surface of liquid aluminium in a closed reaction zone from which air is excluded, the $TiCl_4$ being employed in this example in an amount to obtain a $TiCl_3$ conversion of about 60%, based on the aluminium reacted according to the equation:—



- 10 The vapors issuing from the reaction zone are withdrawn and cooled through the temperature range of 700° C. to 400° C., causing substantially all of the $TiCl_3$ to deposit as a finely divided sublimate substantially free of $AlCl_3$.
- 15 and $TiCl_4$. The sublimate is separately recovered, and the remaining vapor can be treated to recover $AlCl_3$ therefrom, by any desired known method, such as fractional condensation or crystallization of the $AlCl_3$. Surplus $TiCl_4$, lean in respect to aluminium chloride, is recycled to the reaction zone. The $AlCl_3$ can be electrolyzed, if desired, to obtain aluminium useful as the reducing metal, and chlorine usable to chlorinate TiO_2 or scrap or nonductile titanium metal to $TiCl_4$ for use as a starting material also.

- The sublimate of $TiCl_3$ obtained from the reduction is maintained under a countercurrent stream of argon at atmospheric pressure.
- 30 The sublimate is introduced into a horizontal tube, maintaining the protective argon atmosphere, at a temperature of 200° to 300° C. and is gradually heated under the countercurrent stream of argon to a temperature of about 650° C. Most of the reaction occurs in the temperature range of 500° C. to 650° C. The $TiCl_3$ content of the argon entering the disproportionation zone is maintained at a maximum partial pressure of about 10 mm. Hg.
- 40 Except for its $TiCl_3$ content, the argon is highly purified, particularly with respect to oxygen, nitrogen and water vapor. $TiCl_3$ is removed from effluent argon vapors by condensation upon cooling of the vapors, and it is recycled to the reduction step.

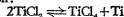
- The product obtained after reaction is completed is a residue of $TiCl_4$ in the form of a black, finely divided crystalline powder. Some titanium trichloride sublimes during the disproportionation reaction and is recycled internally by allowing it to condense on the incoming charge which moves countercurrent to the vapor stream. Thus, the recovery of $TiCl_3$ is substantially stoichiometric, based on the reaction:—



- The finely divided $TiCl_3$ from the above operation is compacted by pressure pelleting in an argon atmosphere in the form of cylindrical rods one-half inch in diameter and one-half inch long. These pellets are heated at atmospheric pressure in a stream of argon having an initial $TiCl_4$ partial pressure of less than 1 to 2 mm. Hg. The pellets are maintained at a temperature of from 700° C. to 1000° C. until the

disproportionation of $TiCl_3$ is essentially complete. Any residual titanium chloride in the product is eliminated by additional heating for two hours at 1000° C. to 1100° C., preferably in a stream of inert gas. The pellets recovered from this heating stage are substantially pure titanium metal and are about one-fourth inch in diameter, a size which is considered very desirable for subsequent melting operations.

This second disproportionation reaction is generally accompanied by some sublimation of $TiCl_4$ at the higher temperatures and by side reactions yielding $TiCl_4$ vapor. Both $TiCl_3$ and $TiCl_4$ are recovered as sublimate from the effluent gases and are recycled to the first heating or disproportionation step. The amount of Ti metal recovered is about 70% of the stoichiometric quantity obtainable, based on the equation:—



All of the above operations are blanketed by argon to prevent atmospheric contamination. The make-up argon used is given a final purification by gettering with Ti metal at 1000° C. to eliminate traces of oxygen, nitrogen and water vapor. In this example, about 30 mols of argon are employed per mol of titanium metal formed, this gas being recycled with addition of a small amount of make-up argon.

EXAMPLE II.

The production of a mixture of lower titanium chlorides by a modified reduction operation is described below:—

The hot reaction vapors, resulting from the reduction of $TiCl_4$ by aluminium as described in Example I, are diluted with 15 to 30 volumes of argon per volume of unreacted $TiCl_4$ vapor, before being cooled. The argon is pre-heated sufficiently to keep the temperature of the diluted vapours above 650° C. The argon used is highly purified except for its $TiCl_3$ content which is equivalent to a partial pressure thereof of about 10 mm. Hg. The diluted vapor mixture is introduced into a condensing zone and is cooled to 350° C. to cause the lower Ti chlorides to deposit. The sublimate produced is moved countercurrent to the gas stream. The sublimate or deposited solid obtained is $TiCl_3$, containing about 20% to 30% $TiCl_4$ and is free from $TiCl_2$ and $AlCl_3$. The crystal of this sublimate is much larger than that of the sublimate recovered according to Example I. The sublimate can be further treated as in Examples I and III to produce titanium metal. However, the larger particle size of this product is particularly advantageous when it is converted to titanium metal by the procedure given in Example IV.

EXAMPLE III.

The production of titanium metal by a 125 modified two-stage diproportionation of $TiCl_3$ and $TiCl_4$ is described below:—

Titanium trichloride, or a mixture of $TiCl_3$ and $TiCl_4$ in powder form, prepared as des-

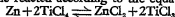
- cribed in Examples I, II and V, is brought into contact with a countercurrent stream of argon and is gradually heated to 200° C. to 300° C., after which the heated material is moved forward under argon atmosphere to the reaction zone which is comprised of a rotating tube inclined downwardly at a slight angle from the horizontal, and the chlorides are there heated to about 850° C., while a stream of argon enters the reaction zone at the opposite end of the tube from the point of introduction of the chlorides and flows countercurrent to the latter. The partial pressure of titanium tetrachloride in the argon thus entering the hot end of the tube or reaction zone does not exceed 1 to 2 mm. Hg. The chloride or chloride mixture is gradually heated to about 850° C. as it progresses through the tube; and the powdered product recovered from the reaction is gray to black in color and contains titanium metal and titanium dichloride. Titanium trichloride and dichloride vapors which are formed recycle internally as described in Example I.
- The powdery product from this operation is compacted into pellets and heated in a stream of argon as described in Example I, but the titanium metal pellets obtained as product of this second heating step are larger and more dense than those obtained according to Example I. The total titanium metal recovered amounts to 80% to 90% of the stoichiometric quantity obtainable. About 40 mols of argon are employed in this example per mol of titanium metal produced, the gas being recycled.

EXAMPLE IV.

- The production of titanium in powdered form is carried out in an alternative procedure, as follows:—
- Titanium trichloride, or a mixture of $TiCl_3$ and $TiCl_4$ crystals, as prepared in Examples I, II or V, is preheated to a temperature of 200° C. to 300° C. and in a stream of argon and is passed through an elongated reaction zone while being progressively and gradually heated to a final temperature of 1000° C. to 1100° C. Argon, in which the partial pressure of $TiCl_4$ does not exceed 1 to 2 mm. Hg., enters at the hot end of the zone and flows countercurrently to the passage of the reacting material. $TiCl_3$ and $TiCl_4$ which sublime during the operation as the temperature increases flow back with the argon stream and condense again, depositing on the charge in the cooler portions of the zone, thus undergoing a continuous internal recycle. The finely divided titanium metal obtained is compressed, in an argon atmosphere, into pellets as feed for subsequent melting and alloying operations. The yield of Ti metal is essentially stoichiometric based on the disproportionation reactions given in Example I, because of the efficient internal recycle of $TiCl_3$ and $TiCl_4$ vapors.

EXAMPLE V.

Liquid zinc and excess vaporous $TiCl_4$ are introduced into a reaction zone, and there reacted, by bringing $TiCl_4$ vapor into contact with the surface of liquid zinc, at a temperature of 800° C. to 850° C. to form a vapor mixture containing $TiCl_3$, $ZnCl_2$, and $TiCl_4$. Sufficient $TiCl_4$ is added in this zone to effect a $TiCl_4$ conversion of about 60%, based on the zinc reacted according to the equation:—

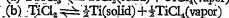
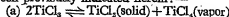


The hot vapors issuing from the reaction zone are diluted with from 15 to 30 volumes of heated argon per volume of unreacted $TiCl_4$ before being cooled to less than 650° C. and are then conducted to a condensing zone where they are cooled to a temperature of about 200° C. The argon employed is highly purified except that it contains $TiCl_4$ equivalent to a partial pressure thereof of about 10 mm. Hg. The solid product recovered from the condensing zone is a brittle heterogeneous mixture of $TiCl_3$ and $ZnCl_2$ crystals and contains substantially all of the $TiCl_3$ and $ZnCl_2$ originally present in the vaporous products from the reaction. The residual vapors from the condensing step are preferably cooled to room temperature to condense and recover the excess $TiCl_4$ present therein, and the argon recovered can be recycled in the operation. $ZnCl_2$ is removed from the $TiCl_3$ — $ZnCl_2$ mixture by extraction with diethyl ether which is a selective solvent for this compound in this mixture. The purified $TiCl_3$ remaining after evaporation of any residual solvent is suitable for conversion to titanium metal of the desired characteristics and is treated according to any of the heating or disproportionation procedures described in the preceding examples.

It is to be understood that the above specific examples are illustrative only and that the process is not limited with respect to the devices, for example, which are mentioned. If desired, $TiCl_3$ may be heated in fluidized state, to disproportionate to $TiCl_4$. In a larger scale operation, it may be preferred to carry out the disproportionation steps by heating agglomerates in one or more vertical towers, and pebble stoves of the kind known to the art may be desired in maintaining the desired temperatures of the gaseous atmospheres. In another method of operation according to the invention, titanium trichloride, which also contains some titanium dichloride in admixture therewith, is introduced into a heating zone and in the presence of a stream of inert gas is gradually heated to a temperature of 1000° to 1100° C., to disproportionate successively the trichloride to dichloride and the dichloride to titanium metal, forming also titanium tetrachloride. The tetrachloride is entrained by and carried off with the stream of inert gas. In such an operation the starting trichloride or mixture of trichloride and dichloride is conducted through the heating zone countercur-

rent to a stream of inert gas and is heated from a starting temperature of about 200° C. to a final temperature of about 1100° C., for example, by introducing the starting chloride into a rotating heating device at the feed end and conducting toward the hotter end of the device, while introducing inert gas as described hereinabove at the hot end of the device and passing it countercurrent to the material being heated. The titanium metal produced is in powder form and is withdrawn and suitably compacted into agglomerates with the aid of pressure, all in the presence of an inert gas. The process, including the reduction and the disproportionation steps, can be carried out batchwise; but it is preferred and more economical to carry the process into operation in a continuous manner.

It is believed that the disproportionation process of the present invention proceeds according to the following equations, as has been previously indicated herein:—



and each of these reactions has an equilibrium vapor pressure which is below atmospheric under the conditions of the reaction. By passing a stream of inert gas, unsaturated with respect to $TiCl_4$, over the reacting mass, the vaporous $TiCl_4$ is removed from the reaction zone, thus displacing the equilibrium and causing the reaction in each case to proceed to substantial completion.

The first disproportionation step forms predominantly $TiCl_3$, but a minor amount of Ti metal can also be formed thereby; and this is not disadvantageous because, in fact, stronger and denser pellets are obtained when finely divided $TiCl_3$ is compacted under pressure in intimate interdispersion with finely divided titanium metal so produced. The preferred mol ratios of inert gas to titanium metal produced have been found in the above specific embodiments of the invention to be from 20 to 50.

All reaction vessels are suitably gas-tight of course, for at least two reasons: (1) to preserve the inert gas, e.g. argon, atmosphere without excessive losses of this gas, and (2) to prevent loss of volatilized lower halides while ensuring complete reaction of the same. Oxygen and nitrogen of the air are also excluded in this manner. It is essential to carry out the reduction of $TiCl_4$ to $TiCl_3$, where this step is practised, in the absence of air or other reactive gas also, to avoid contamination of the $TiCl_3$ with oxygen, nitrogen or water vapor. Preferably, the total pressure in the system is slightly above atmospheric to prevent inward diffusion of air. As stated above, reduction of $TiCl_4$ to $TiCl_3$ by means of a molten reducing metal which forms a chloride of the volatility characteristics noted hereinabove is especially advantageous because purification of $TiCl_3$ is simultaneously effected by reason of the fact that undesired components or contaminants

or impurities, for example, metal oxides, are not volatilized and remain behind in the reduction zone. A temperature of from 700° C. to 1000° C. in the second heating or disproportionation is advantageous not only to ensure complete reaction but to enable use of more readily available materials of construction.

In the specification and claims, all percentages and parts are by weight except as otherwise indicated. The pressures shown are in millimetres of mercury, and the partial pressures of $TiCl_4$, where shown, are original partial pressures, i.e. of the entering gas stream.

What we claim is:—

1. A process for producing ductile titanium from titanium chloride which comprises heating titanium trichloride in the presence of a stream of inert gas at a temperature of from 550° C. to 650° C. to form titanium tetrachloride and titanium dichloride, separately recovering the titanium dichloride, heating the titanium dichloride in the presence of a stream of inert gas as from 700° to 1100° C. to form titanium metal and titanium tetrachloride, and separately recovering the titanium metal.

2. A process as claimed in Claim 1 wherein the inert gas employed is argon.

3. A process as claimed in Claim 2 wherein the titanium trichloride is heated in a stream of argon containing not over 10 mm. original partial pressure of titanium tetrachloride.

4. A process as claimed in Claim 2 or 3 wherein the titanium dichloride is heated in a stream of argon containing not over 2 mm. original partial pressure of titanium tetrachloride.

5. A process as claimed in Claim 4 wherein the stream of argon contains not over 1 mm. original partial pressure of titanium tetrachloride.

6. A process as claimed in any of the preceding claims in which the recovered titanium dichloride is formed under pressure and in the presence of an inert gas, into agglomerates which are then submitted to the second heating step to form titanium tetrachloride and titanium metal in the form of compact agglomerates.

7. A process for producing ductile titanium which comprises introducing into a reduction zone, maintained at a temperature of from 750° C. to 950° C., a reducing metal adapted to form a metal chloride volatile at such temperature and having a condensation point lower than that of titanium trichloride, introducing into said zone in contact with the metal a stream of titanium trichloride and reacting the latter to form a gaseous mixture containing titanium tetrachloride, titanium trichloride and a chloride of the reducing metal, withdrawing a stream of the gaseous mixture and cooling it to 450° C. to 600° C. to deposit solid titanium trichloride, separately recovering the trichloride and introducing it into a disproportionation

- tionation zone, heating the trichloride in the disproportionation zone in the presence of a stream of inert gas to from 550° C. to 650° C. to form titanium dichloride and vaporous titanium tetrachloride separately withdrawing the vaporous titanium tetrachloride, heating the titanium dichloride to from 700° C. to 1100° C. in the presence of a stream of inert gas to form vaporous titanium tetrachloride and solid titanium metal, and separately recovering the titanium metal.
8. A process as claimed in Claim 7 wherein the inert gas is argon.
9. A process as claimed in Claim 7 or 8 wherein the reducing metal is aluminium.
10. A process as claimed in Claim 7 or 8 wherein the reducing metal is zinc.
11. A process as claimed in Claim 7 or 8 wherein the reducing metal is titanium.
12. A process for producing ductile titanium which comprises continuously introducing excess titanium tetrachloride into a reduction zone in the absence of air, introducing molten aluminium substantially free of nitrogen and oxygen into the reduction zone, maintaining the zone at a temperature of from 750° C. to 950° C. and causing the aluminium and titanium tetrachloride to react to form aluminium chloride and titanium trichloride and a minor portion of titanium dichloride, continuously withdrawing a vapour stream containing TiCl_4 , AlCl_3 , titanium trichloride and titanium dichloride from the reaction zone, admixing an inert gas with the vapour stream, cooling the mixture to from 450° C. to 600° C. to condense the titanium trichloride and dichloride, separately recovering the last-mentioned titanium chlorides and introducing them into a first disproportionation zone, heating the chlorides in the first disproportionation zone to from 550° C. to 650° C. to convert the titanium trichloride to titanium dichloride and vaporous titanium tetrachloride, separately recovering the titanium dichloride and compacting it into agglomerates, introducing the agglomerates into a second disproportionation zone and heating therein, in a stream of inert gas, at from 700° C. to 1000° C. to form titanium and titanium tetrachloride, and separately recovering the titanium in compacted form.
13. A process as claimed in Claim 12 wherein the titanium chlorides are heated in the first disproportionation zone at from 575° C. to 625° C.
14. A process as claimed in Claim 12 or 13 wherein the titanium chlorides are compacted into agglomerates before introduction into the first disproportionation zone.
15. A process as claimed in Claim 12, 13 or 14 wherein the inert gas is argon.
16. A process as claimed in Claim 15 wherein the argon in said first disproportionation zone contains not over 10 mm. partial pressure of titanium tetrachloride and the argon in the second disproportionation zone contains not over 2 mm. partial pressure of titanium tetrachloride.
17. A process as claimed in Claim 16 wherein the argon in the second disproportionation zone contains not over 1 mm. partial pressure of titanium tetrachloride.
18. A process as claimed in Claim 15, 16 or 17 wherein a total of from 20 to 50 mol weight of argon per mol weight of titanium metal produced is employed.
19. A process as claimed in any of the preceding Claims 12 to 18 wherein from 5 to 10 volumes of inert gas per volume of vapour are admixed with the vapour stream withdrawn from the reduction zone.
20. A process for making ductile titanium which comprises introducing titanium trichloride into a heating zone, gradually heating the trichloride to a temperature of 1100° C. while passing a stream of inert gas through the heating zone to form finely divided titanium metal, and removing the metal from the zone and compacting into agglomerates under pressure in the presence of inert gas.
21. A process for making ductile titanium metal substantially as hereinbefore described.
22. Titanium metal when produced by a process substantially as claimed in any of the preceding claims.

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